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STUDY OF CONSOLIDATION FEATURES FOR FRAGMENTALLY NANOSTRUCTURED HARD METAL COMPOSITES

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The results of experimental studies combined with modeling and prediction methods for the properties of hard metal composites show that modification with additives of ceramic nanoparticles and composite powders (WC-Co) allows to control microstructure parameters and provides the increase in binding durability and the level of physicomechanical properties of a hard alloy in general. Simultaneous complex application of submicrocrystalline WC carbides coated with Co layer and alloying additives of Al_2O_3 *nanoparticles – grain growth inhibitors of the main phase, can be considered as the most perspective direction of nanostructured hard metal with increased hardness, strength and crack resistance production. The coating of carbide particles with a binder layer is an effective starting method that allows to obtain a volumetric billet with maintaining the unique properties of the initial nanopowders and ensures a uniform distribution of the phases (WC, Co,* Al_2O_3*). Such a multiphase fragmented nanostructured composite is characterized by additional heterogeneity, determined by differences in size and elastic phases properties. By combining the sizes and properties of the phase components in such a heterogeneous composite, it is possible to provide an increase in the fracture energy, i. e., Palmkvist crack resistance up to 16–18 MPa* $m^{1/2}$ *(due to inhibition on nanoparticles inclusions, stress reliefs and changes in intercrystalline crack trajectory, its length decrease). Based on the proposed stereological models and the experimentally established relationships between composition and microstructure parameters, the required volume concentrations of nanoparticles additives and composite powders (WC–Co) were determined.*

Keywords: hard metal composites, nanopowders of ceramic, inhibitors, composite carbides, modeling and microstructure parameters, fracture resistance.

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ИЗУЧЕНИЕ ОСОБЕННОСТЕЙ КОНСОЛИДАЦИИ ФРАГМЕНТАРНО НАНОСТРУКТУРИРОВАННЫХ ТВЕРДОСПЛАВНЫХ КОМПОЗИТОВ

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Результаты экспериментальных исследований в сочетании с методами моделирования и прогнозирования свойств твердосплавных композитов показывают, что модифицирование с помощью добавок керамических наночастиц и композиционных порошков (WC–Co) позволяет управлять параметрами микроструктуры и обеспечивает повышение прочности связующего и уровня физико-механических свойств твердого сплава в целом. Одновременное комплексное применение субмикрокристаллических карбидов WC, покрытых слоем связки Co, и легирующих добавок наночастиц Al_2O_3 *– ингибиторов роста зерна основной фазы, можно рассматривать как наиболее перспективное направление производства наноструктурированных твердых сплавов с повышенной твердостью, прочностью и трещиностойкостью. Покрытие карбидных частиц слоем связки является эффективным стартовым методом, позволяющим получать объемные заготовки с сохранением уникальных свойств исходных нанопорошков, и обеспечивает равномерное распределение фаз (WC, Co,* Al_2O_3*). Такой многофазный фрагментарно наноструктурированный композит характеризуется дополнительной гетерогенностью, определяемой различиями размеров и упругих свойств фаз. Комбинируя размеры и свойства фазовых составляющих в таком гетерогенном композите, можно обеспечить увеличение энергии разрушения, т. е. трещиностойкости, по Палмквисту до 16–18 МПа* $м^{1/2}$ *(за счет торможения на включениях наночастиц, релаксации напряжений и изменения траектории интеркристаллитной трещины, уменьшения ее длины).*

На основе предложенных стереологических моделей и экспериментально установленных взаимосвязей между составом и параметрами микроструктуры были определены требуемые объемные концентрации добавок наночастиц и композитных порошков (WC–Co).

Ключевые слова: твердосплавные композиты, нанопорошки керамики, ингибиторы, композитные карбиды, моделирование и параметры микроструктуры, трещиностойкость.

Introduction. The analysis of accumulated information on scientific research in the field of new structures and hard-alloy composites manufacturing techniques development, production practice and application of various functional purpose products shows that special attention is paid to the use of powder materials components in a composite structure in the nanocrystalline state.

The conventional global trend in the hard-alloy composites structure and properties improving is formation in them a superfine-grained structure with carbide phase sizes less than 300–400 nanometers. The problems of hard alloys quality improvement can be efficiently solved due to their nanostructuring by tungsten carbide nanodimensional powders use. It is well known that when using traditional methods of consolidation for obtaining high density of a sintered composite, high temperature and sintering holding time are necessary and lead to the initial sizes increase and to carbide grains growth [1–4]. Simultaneous use of nano and submicrocrystalline carbides and alloying additives of grain growth inhibitors of the main phase nanoparticles can be considered as the most perspective direction of nanostructured hard alloys with the increased hardness, durability and crack resistance production, which has to increase product endurance under conditions of heavy shock, thermomechanical loading [5] The main inhibitors are chrome carbides, vanadium, niobium, tantalum, titanium. Doping is carried out by various methods, for example, such as chemical, mechanical (high-energy spherical grind), etc. [3]. Forming the complex carbides with the main carbide phase or being dissolved in cobalt, alloying elements influence not only on a microstructure, but also on mechanical and operational characteristics of an alloy [6–8].

A preliminary coating layer binding on carbides, i. e. producing composition powders in various ways, such as dusting, mechanical coating, coprecipitation, consecutive chemical reactions, two-stage processing, etc. can be an efficient processing method as well. The coating of carbide particles with a binding layer is the starting method which allows to get volumetric billet maintaining the unique properties of initial nanopowders [9–11]. Matrix solid phase and covering-binding material are initially homogeneously distributed on the volume of a composite particle, so the properties uniformity of initial powders structure fragments is relayed on all composite volume. Nanodimensional cobalt film presence on carbides powders provides sintering temperature decrease and in combination with high speeds of heating and the existence of inhibiting nanoparticles additives in the structure prevents carbide grains growth [3; 12–15].

Additional modifying by additives of nanoparticles provides the increase in binding durability and the level of physicomechanical properties of a composite in general. Such polyphase fragmentary nanostructured composite is characterized by additional heterogeneity determined by distinctions of the sizes and resilient properties of phases [2]. The range of such nanostructured hard metals possible use will only extend as such modifying changes the surface, chemical and reactionary processes at homogenization and as a result, structural parameters and properties of a composite in general.

Materials and methods. The morphology and microstructure of powders and sintered materials were investigated with the scanning submicroscopy (SEM) of JEOL JSM-7001F use. A particle size distribution of initial and mixed powders were defined by the method of laser diffraction SALD-7101 Shimadzu of the scanning supermicroscope. Samples microstructure was investigated on polished surfaces by means of scanning electron microscopes Hitachi “TM1000” and JEOL JSM-7500FA. The structure and the nature of fracture surfaces were analyzed with the JAMP 9500F microscope use. The X-ray diffraction analysis was carried out on the D8 ADVANCE device. Mechanical propeties determination was performed: Vickers hardness of HV30 with a hardness gage (ABK-A, Akashi) use at 30 kgfs loading; crack resistance K1C dimpling by the Palmkvista method; durability by the three-point bending method on the Shimadzu AG-IS 100 kN; studying of wear-resistance according to the ASTM B611-85 standard.

The nanopowders received by the shock-wave synthesis method or the method of electroexplosion were used as additives for hard alloys modifying. The powders morphology is shown on fig. 1, average particle size in the range from 0.067–of 0.1 microns for Al_2O_3 (*a*, *b*); 0.008 microns for ZrO_2 (Y_2O_3). Composition powders (WC–Co) obtained by complex application of chemical and microwave synthesis methods [10] with 0.2–0.4 microns size (fig. 1, *c*).

Results and discussion. Hard-alloy composites investigated in the work are composite materials, heterogeneous in structure, at least, with one phase showing nanomaterial properties**.** When developing structures, manufacturing techniques and numerical assessment methods of new three-phase hard-alloy composites generation composites formed by a combination of carbides grains (including plated by a binding metal layer), actually binding with the distributed on its volume modifying nanoadditives of oxides, nitrides proceeded from the following assumptions and prerequisites:

– when sintering the prevention of carbide grain growth at the expense of nanoparticles inhibitors additives is provided;

– the distribution of the main phases (a carbide basis, binding, and the nanoparticles distributed on binding volume nanoparticles) is homogeneous, uniform in structure;

– submicronic carbide grains are located at a well predictable distance therefore the package density of a three-phase composite can be regulated (simulated) proceeding from a ratio of micron carbide volume fractions (V_m) and nanodispersible (V_f) fraction and their average sizes (d_m, d_f);

– when modelihg it is necessary to consider differences in a kinetics of mass transfer and reactivity of phase components in a sintering process.

In works [13–15] it was shown that the effectiveness of hard alloys modifying by Al_2O_{3f} nanoparticles essentially depends on sizes, concentration and volume fractions of all composite WC–Co–Al_2O_3(ZrO_2) components.

At the random nature of void filling between carbide grains various structural fragments created by oxide-coated particles which have various degree of contact and internal microporosity can be formed. Conditionally fragments between carbide grains can be presented in the form of three main types of structures – their analytical (model) description compared to the results of the microstructure experiment studies and properties results are given below.

1. The single isolated inclusions of nanoparticles. At small concentration of nanoparticles additives in the local volume of a cobalt layer the fragments presented in fig. 2 are formed.

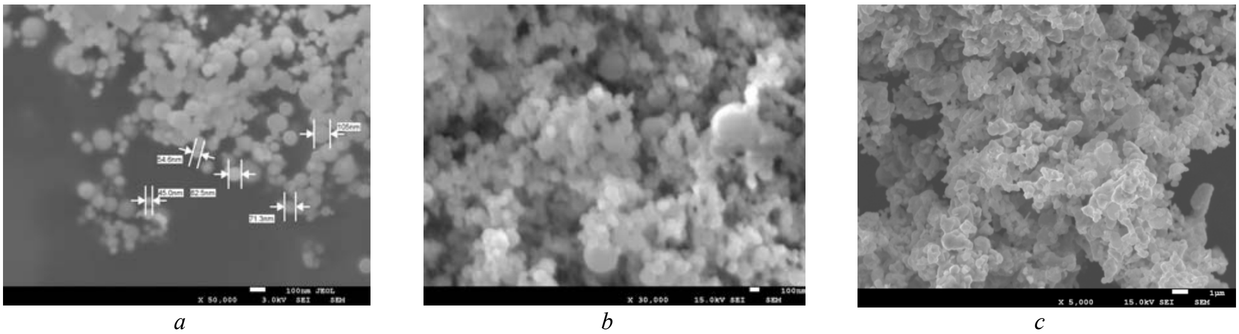


Fig. 1. SEM nanopoweder morphology: *a* – aluminum oxide; *b* – circonium oxide; *c* – tungsten carbide composite particles coated with Co-layer (WC–Co)

Рис. 1. SEM-морфология нанопорошков: *а* – оксид алюминия; *б* – оксид циркония; *в* – композитные частицы карбида вольфрама, покрытые слоем кобальта (WC–Co)

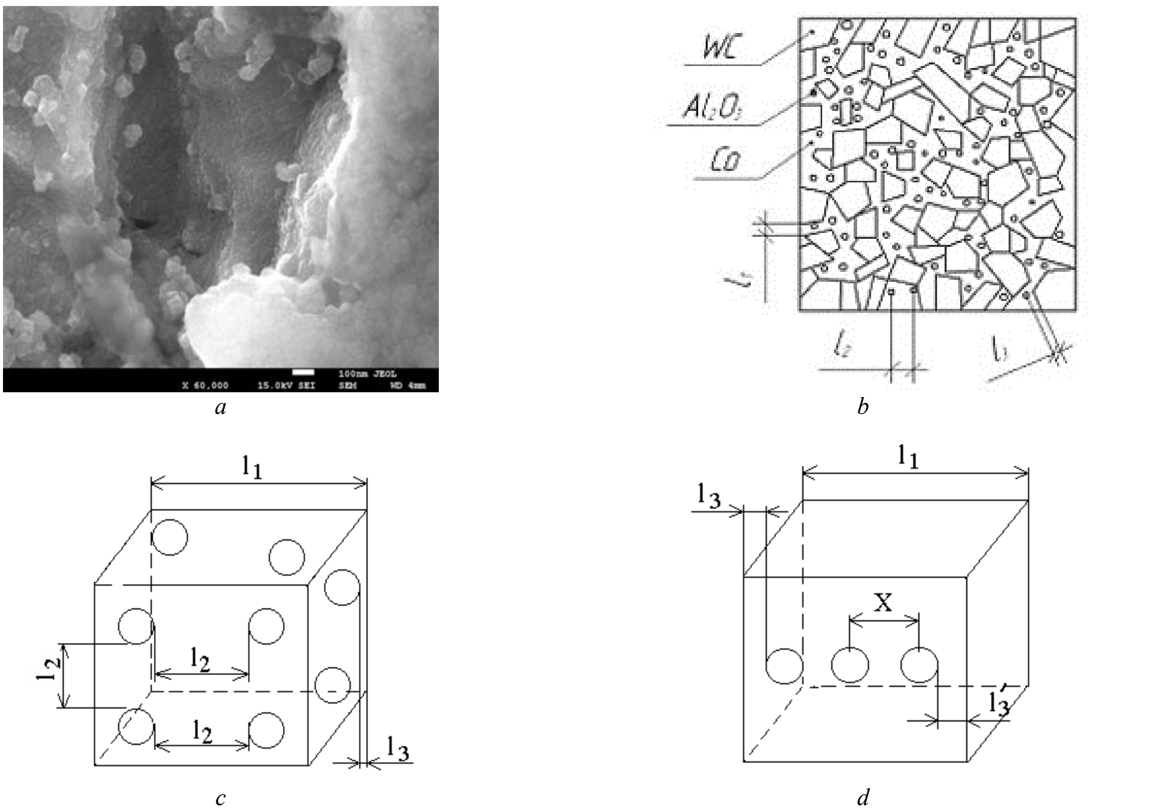


Fig. 2. Geometric model of a hard alloy modified by nanoparticles: *a* – structure (fracture) fragment between carbide grains of a hard-alloy composite including Al_2O_3 nanoparticles; *b* – microstructure scheme; *c*, *d* – single volumes of cobalt binding

Рис. 2. Геометрическая модель твердого сплава, модифицированного наночастицами: *а* – фрагмент структуры (излома) между карбидными зернами твердосплавного композита с включениями наночастиц Al_2O_3; *б* – схема микроструктуры; *в*, *г* – единичные объемы кобальтового связующего

Realization of this kind of fragments a WC–Co-nanoparticle composites structures is optimum from the point of view of the known mechanisms of dispersion metals hardening [2; 15]. Injected into a binding layer isolated and statistically uniformly distributed nanoparticles promote decrease of its thickness $\lambda_{эфф} = f(l_1, l_2, n_2)$ (fig. 2, *a–c*), which has to provide an increase of binding durability and, as result, hard-alloy composites in general according to mechanics of phases provisions. The efficient thickness of a cobalt layer choice $\lambda_{эфф}$ was made on the basis of probability approach on the model more detailed described in [13–15] and various optional versions of a crack distribution through binding layers by width of l_1, l_2, l_3, which sizes depend on nanoparticles additives contents and sizes. At the same time it was supposed that the material in unit volume of a cobalt binding (l_1^3) between carbide grains modified by nanoparticles, is dispersiblly strengthened according to the known Orovana mechanisms, i. e. durability of such fragment of the binding material modified by nanoparticlesadditives above, than at basic material cobalt:

$$\sigma'_B = 480 + \frac{1550}{\lambda'}, \text{ а } \lambda' = \lambda_{эфф}. \qquad (1)$$

The destruction viscosity (crack resistance) of such fragmentary nanostructured hard-alloy composite can be determined by the formulas offered in works [16; 17] and adapted to the hard-facing alloys modified by nanoparticles:

$$K_{1c} = \left\{ \frac{R \cdot (\lambda + d_m) \cdot \sigma'_B \cdot V_m \cdot E'}{C_1} \right\}^{\frac{1}{2}}, \qquad (2)$$

where R – empirical reduction coefficient; d_m – the average size of carbide grain; V_m –volume ratio of carbide fraction; E' – the given elastic modulus; C_1 – contact ability of carbide edges.

The results of calculations for the offered model show satisfactory convergence of calculation data with the experimental [14].

By the experimental methods it was determined that ceramics nanoparticles Al_2O_{3f} in the quantity of 0,05–0,25 % on weight, not only dispersiblly strengthen a cobalt layer (H_μ microhardness, measured by the micronanohardness testing method, increases up to 22.01 GPa), but also provide flexure strength increase (to 25 %) – crack resistance according to Palmkvista (up to 50 %) (fig. 3), decrease in an abraser wear ~ 1.5 times. Minimum values of a wear are observed approximately in the same areas of additives (~ 0.25 % of masses.), which provide durability increase.Tthe offered model calculations results show satisfactory convergence of calculation datas with experimental (fig. 3) [18].

Additional contribution to material wear resistancel increase is brought, apparently, by the increased resilience to an attrition of the aiuminium oxide itself (H_μ Al_2O_3 – 18–20 GPa). Substantially increase in the common level of strength properties is explained by the inhibiting effect of nanoparticles additives, the average size of carbide grain monotonically decreases with increase in their concentration [19]. Material hardness and density values do not differ significantly from basic material and are at the level: but values of a microhardness of binding layer material – cobalt, which was estimated by means of nanomicrohardness gage increase as the known effect of dispersible hardening at the level of structure fragments is implemented (Co – Al_2O_3), slightly different.

2. Agglomerates from nanoparticles. Electronic and microscopic research shows that actual parameters of a hard-alloy composite microstructure differ from the geometrical model presented in item 1. It is quite understandable on the assumption of physical reasons. At increase in nanoparticles concentration in local volumes because of poor uniformity of components interfusing, their contact ability degree increases and there occurs a formation of units with developed internal microporosity. During a unequigranular hard-alloy composites sintering process, the change of interphase energy happens first of all due to nanodisperse phases specific surface area decrease that can be followed by their agglomerating to larger micron formations and possible subsequent coagulation (fig. 4).

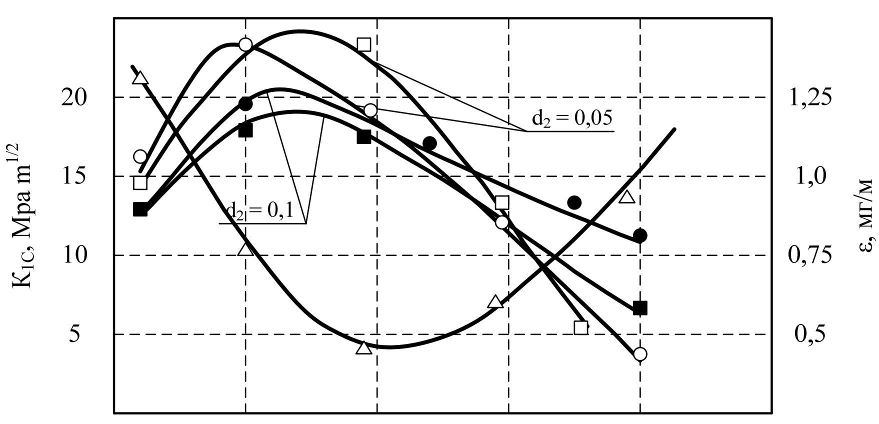


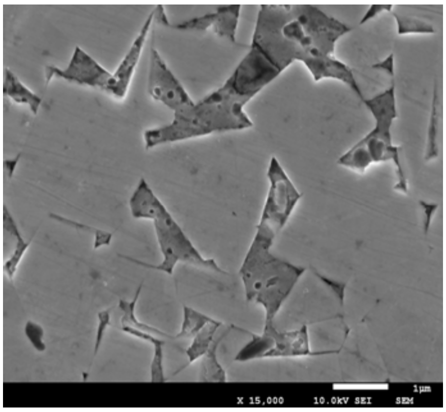
Fig. 3. Nanoparticles size (d_2) vs crack resistance (K_{1C}) of WC–Co – nano Al_2O_3 composite: (● – calculation; □ – experiment) and wear rate

Рис. 3. Влияние размера наночастиц (d_2) на трещиностойкость (K_{1C}) композита WC–Co – нано-Al_2O_3:(● – расчет; □ – эксперимент) и интенсивность износа

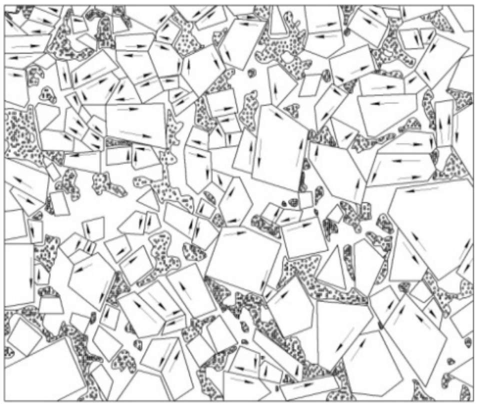
However the noted structural metamorphoses are, to some extent, inevitable at traditional widely applicable in hard alloys production mixture-preparation methods.

When reaching critical concentration of some nanoparticles and emergence of pressure between carbide grains at a liquid-phase sintering, manifestation of self-organization effects is revealed – a volume space structural grid formation. Its basic elements are, apparently, contacts between nanoparticles and the nanoparticles in total forming the exact regular space cells with sizes of 100 nanometers in total (fig. 5, *b*). The agglomerates formed by ceramics nanoparticles become nanostructured i. e. pass into a totally new state. Emergence of such space fragments and transitions from free-dispersible to the bound-dispersible (aggregated) systems also a composite properties change. It can be explained on the basis of the well-known physical principles of ultradispersion mediums sintering theory, including nanostructural hard alloys [1–5; 20]. The existence of such fragments is illustrated by the results of a microstructure research (fig. 5). Besides, there can be formed crystal grains of α-phase Al_2O_3 inclusions (fig. 5, *a*), micron sizes, formed at the increased compounds density of a nanophase and as a result of sufficiently high pressures action in the intercarbide space during a sintering process (about 1370 ºC sintering point is enough for nano Al_2O_3 crystallization).

3. Unequigranular heterogeneous structure. The actual microstructure of the hard-alloy composites modified by nanoparticles is heterogeneous, nonuniform on distribution and morphology of the additional oxide-coated phase created from nanoparticles. Formation of various types of structures (item 1, 2) can occurs at the same time on different mechanisms depending on various nanoparticles concentration in local volumes between the main carbide phase grains. During a sintering process various competing homogenization processes are implemented, their transformations also occur. It is confirmed by the results of own microstructure electronic and microscopic research and of other authors data [1–4; 21]. Typical images of fragmentary nanostructured materials from polished surfaces of samples are provided in fig. 5, 6.



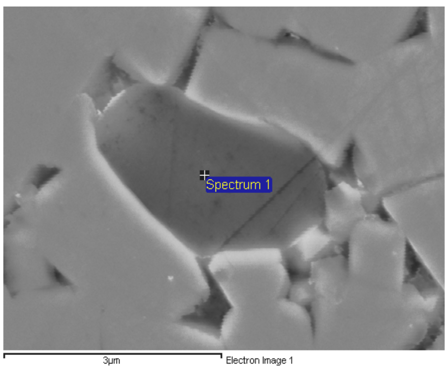
a



b

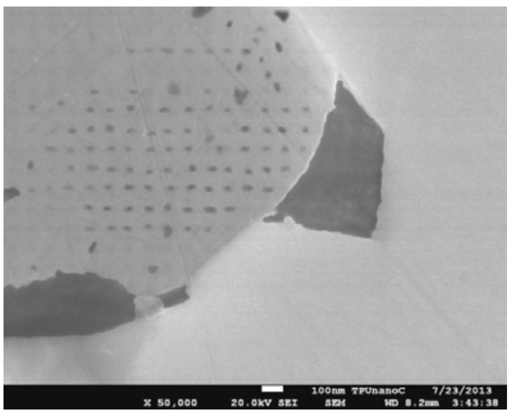
Fig. 4. Nanoparticles distribution within hard-alloy composite WC–Co–Al_2O_3 (nano):
a – concept scheme; *b* – microstructure fragment

Рис. 4. Распределение наночастиц в структуре твердосплавного композита WC–Co–Al_2O_3 (нано):
а – принципиальная схема; *б* – фрагмент микроструктуры



Spectrum	O	Al	W

a



b

Fig. 5. Evolution of agglomerate structures from nanoparticles: *a* – crystallites; *b* – quasi-nanostructured fragment

Рис. 5. Эволюция структуры агломератов из наночастиц: *а* – кристаллиты; *б* – квазинаноструктурированный фрагмент

On the microscopic (micron) level statistically uniformly distributed on material volume basis structural fragments in total (combination) form a new composite of a more complex level. The additional heterogeneity caused by distinctions of resilient phases characteristics describes such polyphase composite. It is revealed in inhomogeneity of a strain-srtess state at a liquid-phase sintering when manufacturing (at phase boundaries, in the course of contraction, consolidation) and at external mechanical impact on the compacted material.

In particular, it is confirmed by material destruction viscosity research data according to the Palmkvista method in combination with a microstructure study. Cracks which are formed in the material as a result of an indentor (a diamond pyramid of Vikkers) introduction, draw attention essentially because they are potential carriers of indirect information on durability, operational material resistance, reflect changes in destruction mechanisms corresponding to various types of structure (fig. 2, 4).

The crack which moves (propagates) mainly on WC interface boundaries – WC, WC–Co slows down (fig. 7, *a*, *b*), relaxes on nanoparticles Al_2O_3, ZrO_2 dispersible inclusions, or on their conglomerates (fig. 7, *c*) distributed on cobalt layers volume.

It is necessary to emphasize in this regard that emergence of discrete cracks approximately corresponds to the area of particles additives up to 0.2 % of masses. Similar changes in destruction mechanisms of the hard-alloy nanostructured composites at cracks propagation are indicated in research results [22; 23].

Thus, combining phase components sizes and properties of in such heterogeneous composite, the energy of destruction increase (increase in trajectory length of an intercrystalline crack) is provided [24]. Despite structure inhomogeneity of an actual three-phase composite and existence of various types of fragments, the common integral level of physicomechanical properties in the field of optimum additives increases research [14; 18].

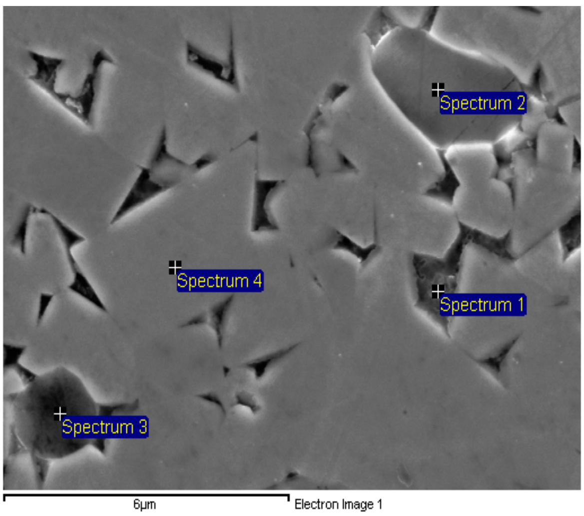
4. Polydisperse material on the basis of composite powders. Based on the positive experimental results and the discovered features of heterophase hard-alloy composites structure formation, the geometrical model (fig. 2) also explicitly described in works [14], was specified and corrected, taking into account the known and new results of calculated and experimental studies of bimodal and polymodal disperse system package density as well.

The offered specified stereological model is quadruple contacting in threes same size composite matrix particles (WC–Co). Carbide phase particles during modeling are conditionally accepted to be spherical. The centers of these spheres are tops of a tetrahedron which edges are formed by radiuses of R_i (fig. 8).

On the basis of the conducted experimental studies the specified stereological model is offered [25]. During its realization the maximal package density and uniformity of composite phase components relative distributionis are provided. The modifying additives of nanoparticles homogeneously distributed in a binding layer promote its thickness decrease $\lambda_{эфф} = f(l_1, l_2, n_2)$ (fig. 8, *a*–*c*) that according to a geometrical model (p. 2.1) has to provide an increase of binding durability and as a result, a hard-alloy composite in general.

A single volume (V_c) of such structure fragment with a particles bimodal distribution by sizes ($\bar{d}_m$, $\bar{d}_f$) can be defined proceeding from the ratio: $V_c = N_m v_m + v_p$, where N_m – a number of carbide particles; v_m – the average volume of carbide particles. Voidage (v_p) between carbide particles proceeding from the known stereology provisions can be accepted equal to $v_p = 0.20776\,(d_m / 2)^3$.

As a way of pressing density increase it is offered to enter tfa nano phase v_f additional volume equal to the volume of voids, i. e $v_p = N_f v_f$. This condition is actually impracticable as the secondary nanoparticles dense packing forms own voids of v_{pf} (fig. 8, *b*), i. e. N_f has to be reduced to N_f* by the volume of v_{pf} which is offered to equate to the volume ratio of metal binding $v_b = v_{pf} =$ $= 0.20776\,(d_f /2)^3$ (the quantity of N_f* particles can be calculated by analogy proceeding from the ratios given above). With this approach to the solution of a composite structure model operation problem its maximal density is provided.



Spectrum	C	O	Al	Co	W
Spectrum 1	13.40	3.65	1.17	74.6	7.25
Spectrum 2	–	58.94	37.08	0.71	3.27
Spectrum 3	–	57.02	31.32	6.16	5.50
Spectrum 4	46.03	–	–	–	53.9

Fig 6. Forming of different structure fragments within heterogeneous hard-alloy composite

Рис. 6. Формирование различных фрагментов структуры гетерогенного твердосплавного композита

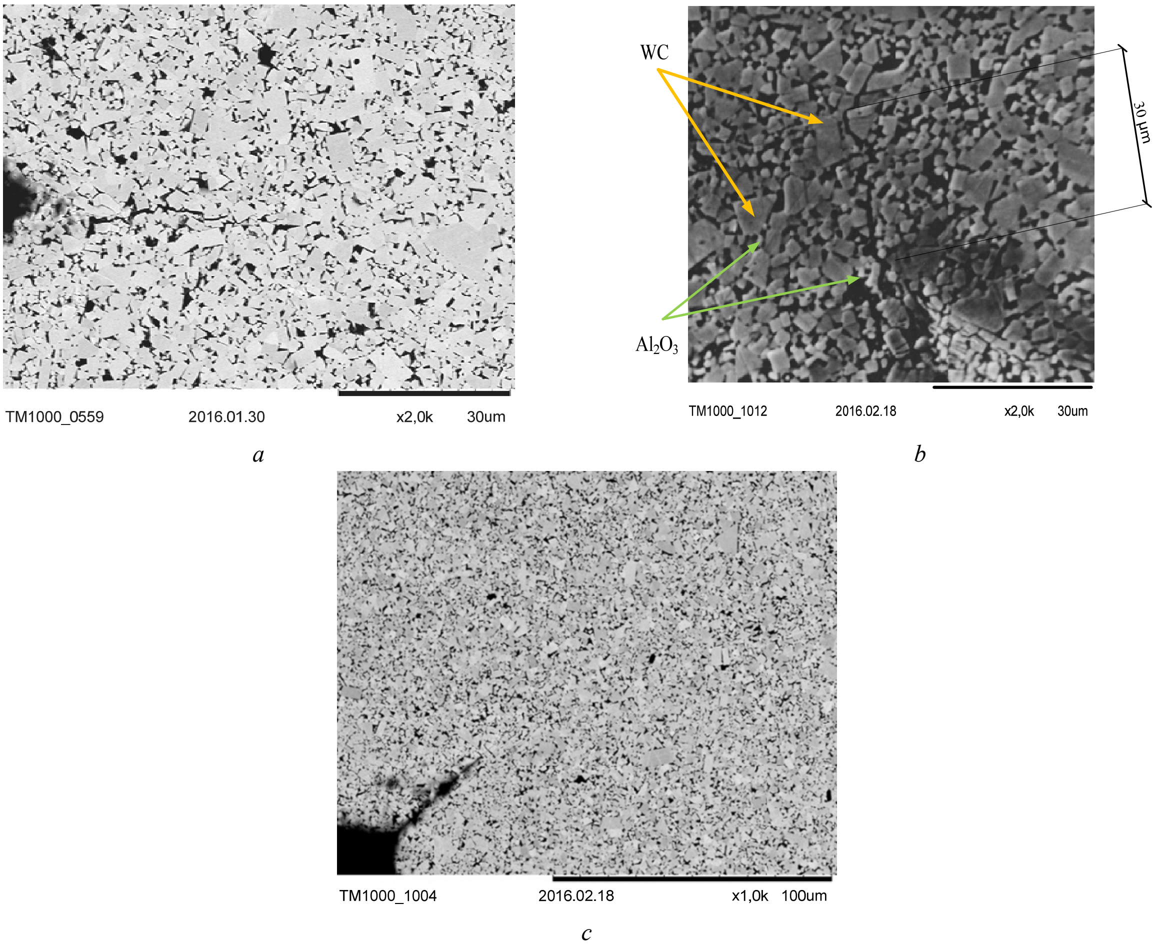


Fig. 7. Crack-propagation pattern due to the Vickers Pyramid dint: (*a*, *b*) – crack stopping at nanoparticle inclusions (binder metal on the surface of polished section has been removed by etching); (*c*) stress relaxation in the front of crack propagation (contrasting etching of the section)

Рис. 7. Характер распространения трещин от угла отпечатка пирамидки Виккерса: *а*, *б* – торможение трещины на включениях наночастиц (металл связки с поверхности полированного шлифа удален травлением); *в* – релаксация напряжений во фронте распространения трещины (контрастное травление шлифа)

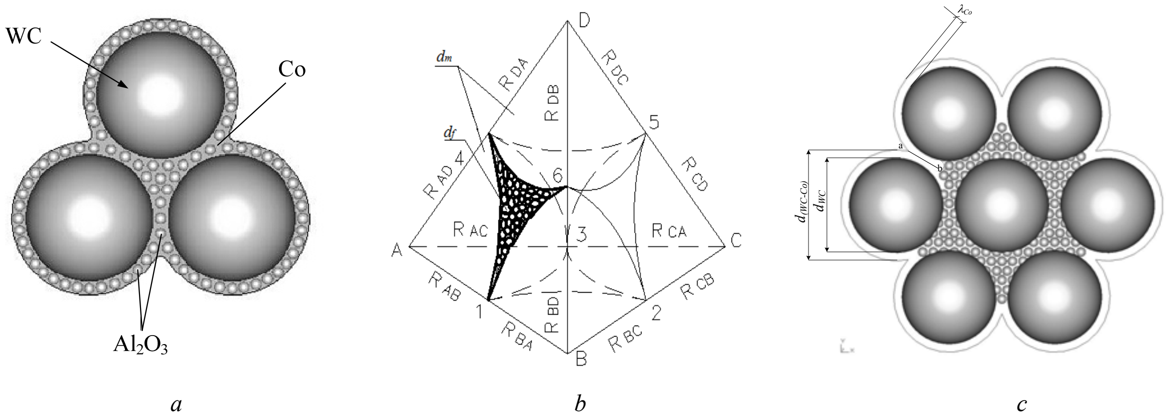


Fig. 8. Stereological model of a three-phase composite:
a – packing scheme; *b* – geometric model of the system d_m(WC–Co) – nano-agents of ceramic d_f (Al_2O_{3f}, ZrO_{2f}); *c* – three-phase structure parameters

Рис. 8. Стереологическая модель трехфазного композита:
а – схема упаковки; *б* – геометрическая модель системы d_m(WC–Co) – нанодобавки керамики d_f (Al_2O_{3f} , ZrO_{2f}); *в* – параметры трехфазной структуры

Composite powders use is expedient, proceeding as well from physical reasons as well, because the existence of a thin-layer binding activates the processes of consolidation, mass transfer at the lower sintering point.

The formation condition in a monolayer sintering process (binding – nanoparticles) and at the same time demands obtaining a hard alloy dense structure from composite powders (WC–Co) demands at "sewing together" of different models, considered in the work, realizations of the following ratios:

$$\beta_0 \cdot \sum_{i=1}^{Nm} \left(d_m + d_f \right)^3 = N_m \cdot v_m + N_m \cdot v_\rho - N_f \cdot v_f, \quad (3)$$

$$v_h = 4\pi((R_m + h)^3 - R_m^3)/3R_m^3, \quad (4)$$

where β_0 – the coefficient defining a form of structure; h – layer thickness of a nanoparticles monolayer with d_f size; v_h – layer volume with h thickness.

Meanwhile, the numerical values of parameters of a composition particle and coat layer thickness from metal binding on composite carbides powders can be defined from a simple ratio:

$$\frac{V_h}{V_{cm}} = \frac{\sigma h}{\bar{d}_m}, \quad (5)$$

where V_{cm} – composite particle volume.

On the basis of a new stereological model (fig. 8) estimating calculations of nanoparticles additives necessary to generate pressings with the greatest package density were made. For particle sizes of a composite carbide phase with sizes in the range of d_m (WC) from 0.3 to 0.8 microns and the sizes of ceramic nanoparticles d_f from 0.008 to 0.1 microns used in the experimental part of work the necessary concentration of nanoparticles additives in mixture composition made $V_f = 0.30$ or about 3 % of masses. The results of experimental studies allowed to specify calculated formulas by means of semiempirical coefficients and to define optimum concentration of nanoparticles additives in the range from 1 to 3 % of masses.

The use of composition submicronic powders (WC–Co) received by various methods [9–11] can be the way of implementation of this kind of heterogeneous structures with the maximal package density and at the same time providing high uniformity of the relative composite phase components distribution. In the experimental part of work the composition powders received a traditional chemical deposition on the carbon carrier in combination with microwave influence [10] (fig. 9) are used.

X-ray phase analysis results showed that the made powder hard-alloy mixtures, alloyed by oxides nanoparticles in the number of 1 %, have the average size of tungsten carbide crystal grains about 150 nanometers. Alloying additive content Increase from 1 to 3 % finds a tendency to decrease of nanoparticles coalescence effects of tungsten carbide when processing in the spherical activator and US- activation [26].

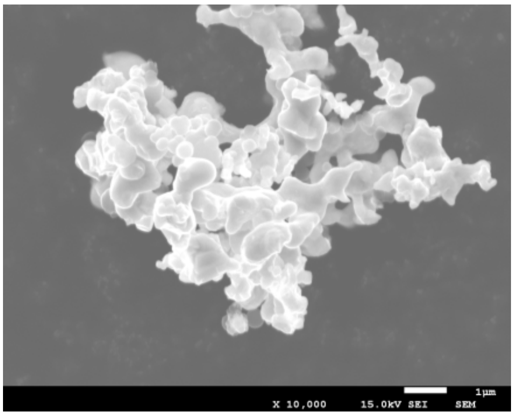
In case of composition layer powders (WC–Co) of the submicronic sizes as a basis and additional alloying of inhibitors nanoparticles additives Al_2O_3 use, the structure created as a result of a simple hard alloy sintering consists of almost isolated carbide grains partially blocked at the expense of a cobalt ductile coat (fig. 10, *a*). The intercarbide space is filled with a composition powders coat layer (Co–WC) and additives of oxides nanoparticles (fig. 10, *a*).

Efficiently influence the processes of such hard alloys structurization is also possible due to the use of the alternate methods of consolidation, intensive plastic and a shear deformation at mixtures formation (for example extrusion or rolling), stage-by-stage stepped heating with withstanding temperatures corresponding to the consolidation mechanisms change, the so-called operated sintering, high-speed and low-temperature compression sintering, electrospark plasma sintering, methods of thermomechanical cycling (which are widely applied for steels and alloys) and thermomechanical ultrasound processing. The physical sense of such influence is that in a peculiar material "buildup", structurization processes activation at consolidation, decrease in the average size and carbide grains contact ability. Finally it will allow to reduce a sintering point and to create and keep more fine-grained structure of a hard alloy composite $WC–Co–Al_2O_3$, $WC–Co–ZrO_2$. Studying of alloys consolidation features on the basis of submicronic composite powders (WC–Co) with initial sizes of carbide grain about 0.8 microns show that intensive contraction occurs already at a temperature 1320–1350 ºC that is on hard-phase sintering stages. These data are well consistent with the results given in works [1; 3]. In temperatures intervals from 1370–1420 ºC there is a partial grain recrystallization of the phase WC to the sizes of 1.5 microns. However at the same time the submicronic carbide phase of initial composite powders in combination with additives of oxides nanoparticles (fig. 10, *a*) remains in a cobalt layer between these carbide grains. Finally, positive structural changes provide additional increase of a strength properties level. Additional experimental studies conducted in collaboration with National Research Tomsk Polytechnic University (TPU) [26] demonstrate that critical threshold concentration cut-off levels of nanoparticles additives in the nanostructured hard-alloy composites *WC–Co-–nano* $Al_2O_3(ZrO_2)$, received by the electrospark plasma sintering method, is 3 % of masses. In total the calculated results (on the model) and the experimental studies (methods of a scanning electron microscopy in combination with the elememt-by-element analysis use and standard methods of physical tests) allowed to realize microstructure parameters with relatively high distribution uniformity of phase components (tungsten carbides grains, a metal binding layer and modifying additives of nanoparticles) on a volume of a hard-alloy composite (fig. 11).

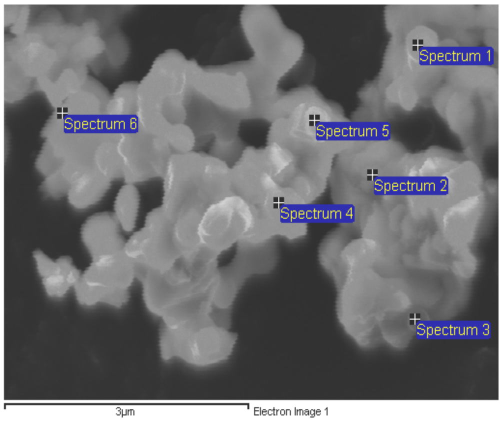
Increase in content of alloying additive to 3 % leads to slowing down of grain growth processes: the average size of coherent scattering area (CSA) for these samples was in the range from 151 to 163 nanometer (fig. 12, *b*). The average size of CSA cobalt bindings according to X-ray analysis does not exceed 22 nanometers [26].

Thus, the received results demonstrate positive influence of nanoparticles additives on properties of reference hard alloys (see the table) that is explained, first of all, by their structural parameters change.

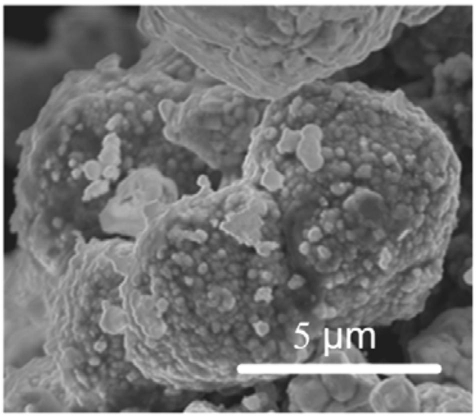
Formation of nanostructural fragments in the volume of a metal cobalt layer provides decrease to the submicronic sizes of its thickness between carbide grains, the effect known in materials science as the effect of dispersible hardening, is implemented.



a



b

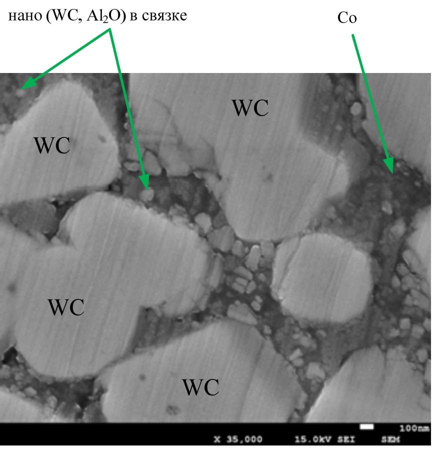


c

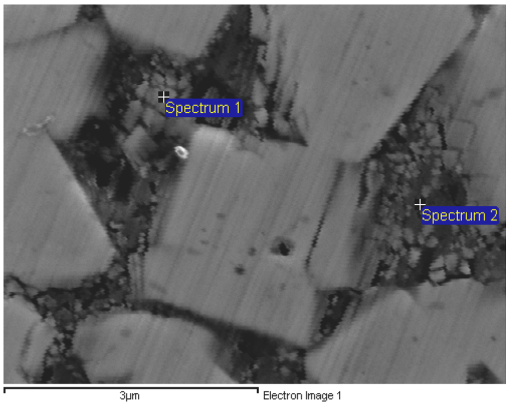
All results in atomic %				
Spectrum	C	O	Co	W
Spectrum 1	76.22	3.35	2.09	18.34
Spectrum 2	61.08	3.93	7.11	27.88
Spectrum 3	86.56	1.48	1.35	10.61
Spectrum 4	73.87	3.36	1.61	21.16
Spectrum 5	73.22	2.61	1.83	22.35
Spectrum 6	80.20	3.71	3.19	12.91

Fig. 9. WC–Co composite powders morphology:
a – microwave synthesis composite powders; *b* – results of powders elementary analysis; *c* – powders (WC–Co) produced by chemical method

Рис. 9. Морфология композитных порошков WC–Co:
а – композитные порошки микроволнового синтеза; *б* – результаты их элементного анализа; *в* – порошки (WC–Co), полученные химическим методом



a



Spectrum	C	O	Co	Al	W
Spectrum 1	24.94	10.44	8.44	1.44	54.74
Spectrum 2	16.89	–	2.56	2.20	78.35

b

Fig. 10. Microstructure of hard alloys obtained from composite powders WC–Co: *a* – SEM; *b* – elementary analysis results

Рис. 10. Микроструктура твердых сплавов полученных из композитных порошков WC–Co: *а* – SEM; *б* – результаты элементного анализа

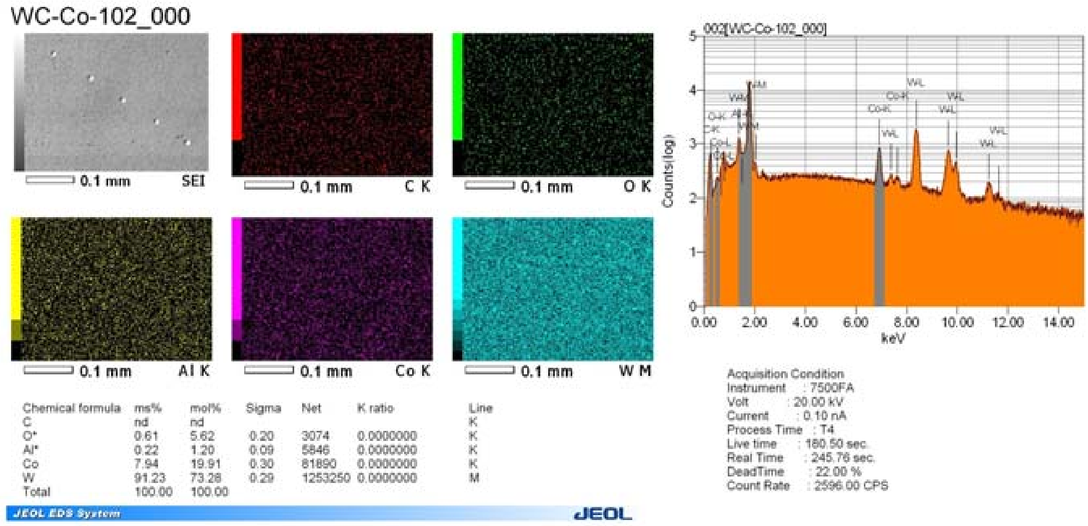
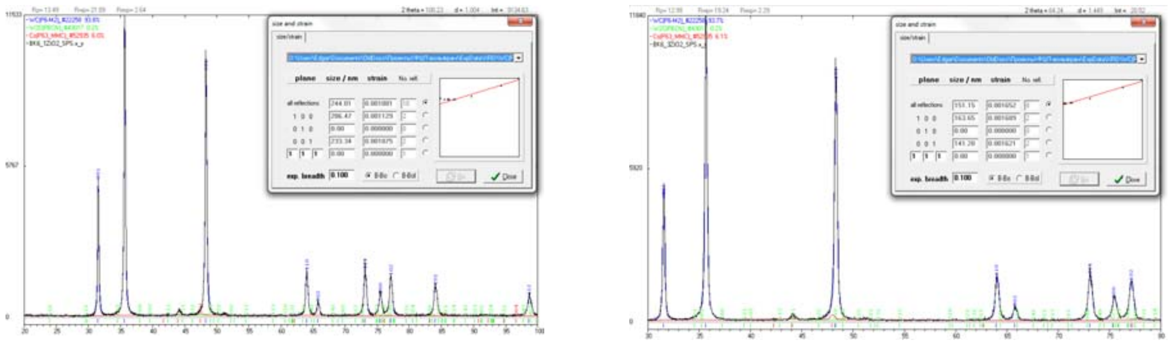


Fig. 11. Electron microscope images: nanostructured hard alloy, EDS map for local deposit of alloying constituent on the surface of hard-alloy composite produced on the basis of micron carbide powders with aluminum oxide

Рис. 11. Электронно-микроскопические изображения наноструктурированного твердого сплава, EDS-карта локального залегания легирующего компонента на поверхности твёрдосплавного композита, изготовленного на основе микронных порошков карбидов с добавками оксида алюминия



a *b*

Fig. 12. X-ray structure analysis of hard-alloy composites consolidated by electro-impulse plasma sintering method using nanoparticle additives: *a* – 1 %; *b* – 3 %

Рис. 12. Результаты рентгеноструктурного анализа твердосплавных композитов, консолидированных методом ЭИПС с количеством добавок наночастиц: *а* – 1 %; *б* – 3 %

Some strength characteristics of hard-alloy composites

Composition of the material		Physicomechanical characteristics		
		Hardness HV, ГПа	Tensile strength at bending R_{bm}, ГПа	Crack resistance K_{Ic}, МПа · м$^{1/2}$
Microcrystalline, ВК15 + Al_2O_3		12.7	2.54	21.6
Microcrystalline, ВК10КС + Al_2O_3		15.1	2.68	19.3
Quasy-nanocrystalline	ВК6	19.5 ± 0.6	2.03 ± 0.1	9.1 ± 0.6
	ВК6 + 2 % ZrO_2	20.4 ± 0.6	2.17 ± 0.1	9.3± 0.7
	ВК6 + 4 % ZrO_2	22.0 ± 0.6	2.09 ± 0.1	9.7

Conclusion. The conducted complex parametrical research results demonstrate that when modifying hard-alloy composites by nanoparticles the principle of “composition-structure-property”, known in materials science, is implemented. In total, the received results of experimental studies in combination with methods of computer modeling and prediction of hard-alloy composites properties, modified by additives of ceramics nanoparticles, provide expansion of opportunities for structure and hard alloys properties operation.

Composite submicronic powders (WC–Co) use in combination with modifying nanoparticles Al_2O_3, ZrO_2 (inhibitors) is an efficient starting method of nanostructured hard-alloy composites quality improvement. The calculated results (on the model) and the experimental studies comparison show satisfactory coincidence of the predicted microstructure parameters and strength properties with the obtained.

References

1. Fang Zak Z., Wang Xu, Taegong Ryu, Kyu Sup Hwang, Sohn H. Y. Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide – A review *Int. Journal of Refractory Metals & Hard Materials*. 2009, Vol. 27, P. 288–299.

2. Andrievski R. A., Glezer A. M. Strength of nanostructures. *Physics-Uspekhi.* 2009, Vol. 52, No. 4, P. 315–334.

3. Panov V. S., Zaitsev A. A. Trends of development the technology ultrafine and nanosized tungsten carbide WC–Co – A review *Proceedings of the universities. Powder metallurgy and functional coatings*. 2014, No. 3, P. 38–48.

4. González Oliver C. J. R., Álvarez E. A., García J. L. Kinetics of densification and grain growth in ultrafine WC-Co composites. *Int. Journal of Refractory Metals and Hard Materials*. 2016, Vol. 59, P. 121–131.

5. Rempel' A. A., Kurlov A. S., Tsvetkov Yu. V. *Tungsten carbide nanopowder for WC–C_o hard alloys, Proceedings of the Fourth All-Union Conference on Nanomaterials.* Moscow, IMET RAN Publ., 2011, P. 71.

6. Sun L., Jia C., R. Lin Cao, Lin C. Effects of Cr_3C_2 additions on the densification, grain growth and properties of ultrafine WC–11Co composites by spark plasma sintering. Sun, *Int. J. Refract. Met. Hard. Mater*. 2008, Vol. 26, P. 357–361.

7. Huang S. G., Liu R. L., Li L. NbC as grain growth inhibitor and carbide in WC–Co hardmetals. *International Journal of Refractory Metals & Hard Materials.* 2008, No. 26, P. 389–395.

8. Cholsong P., Ji L., Zhimeng G. Microstructure and properties of ultrafine WC-10Co composites with chemically doped VC. *Rare metals.* 2011, Vol. 30, No. 2, P. 183–188.

9. Vollath D., Szabo D. V. Coated nanoparticles: A new way to improved nanocomposites. *Journal of Nanoparticle Research.* 1999, Vol1, P. 235–242.

10. Nikolaenko I., Kedin N., Shveikin G. Synthesis of ultrafine powder (W, Ti) C by microwave heating in a stream of argon. *International Journal of Materials Research.* 2014, Vol. 105, No. 12, P. 1232–1235.

11. Essaki K., Rees E. J., Burstein G. T. Synthesis of Nanoparticulate Tungsten Carbide Under Microwave Irradiation. *J. Amer. Ceram. Sos.* 2010, Vol 93, No. 3, P. 692–695.

12. Yamamoto T., Ikuhara Y., Watanabe T. et al. High resolution microscopy study in Cr3C2-doped WC–Co. *Journal of Materials Science.* 2001, Vol. 36, P. 3885–3890.

13. Gordeev Y., BucaemskyA., Seher G., Teremov S. *Powder metallurgy world congress and exhibition*. 1998, Vol. 4, P. 140–146.

14. Gordeev Yu., Abkaryan A., Zeer G. Design and research of cemented carbides and ceramic composites modified by nanoparticles. *Advanced Materials*. 2012, No. 5, P. 76–88.

15. Gordeev Yu., Abkaryan A. [Possibility of increasing the strength of carbide materials and operational stability of the cutting tool through the use of thermomechanical processing] *Stanki i instrument.* 2013, No. 3, P. 30–34.

16. Nakamura M., Gurland J. The fracture toughness of WC–Co twoophase alloys: A preliminary model, *Metall. Trans.* A. 1980, Vol. 11, No. 1, P. 141–146.

17. Godse R., Gurland J. Applicability of the critical strength criterion to WC–Co, *J. Mater. Sci. Eng. A*. 1988, Vol. 106, P. 331–336.

18. Gordeev Yu., Abkaryan A., Zeer G., Lepeshev A. [Effect of alloying additions of ceramic nanoparticles on the structural parameters and properties of hard alloys]. *Vestnik SibGAU*. 2013, No. 3(49), P. 171–181 (In Russ.).

19. Gordeev Y. I., Abkaryan A. K., Binchurov A. S., Jasinski V. B., Vadimov B. H. [Design and investigation of hard metalls composites modyfied by nanoparticles and thermomechanical treatment with a high level of mechanical and operating properties]. *Vestnik SibGAU.* 2014, No. 4 (56), P. 209–218 (In Russ.).

20. Kurlov A. S. Vacuum sintering of WC-8 wt.% Co hardmetals from WC powders with different dispersity. *International Journal of Refractory Metals and Hard Materials.* 2011, No. 29 (2), P. 221–231.

21. Gordeev Y. I., Abkaryan A. K., Binchurov A. S., Jasinski V. B. Design and Investigation of Hard Metal Composites Modified by Nanoparticles. *Advanced Materials Research*. 2014, Vol. 1040, P. 13–18.

22. Dvornik M. I, Mikhaylenko Ye. A. [Modeling the process of crack propagation in submicron and nanostructured hard metals]. *Mechanics of composite materials and structures*. 2014, Vol. 20, No. 1, P. 3–15.

23. Dvilis E. S., Khasanov O. L., Bikbaeva Z. G., Polisadova V. V., Struts V. K., Omarov G. Z., Khasanov A. O. Pattern of the B4C Ceramics Surface Deformation at Local Loading. *Advanced Materials Research*. 2014, Vol. 872, P. 60–64.

24. Pozdnyakov V., Glezer A. [Structural mechanisms of destruction of nanocrystalline materials]. *Solid State Physics*. 2005, Vol. 47, No. 5, P. 793–800.

25. Gordeev Y. I., Abkaryan A. K., Binchurov A. S., Lepeshev A. A., Yasinski V. B. Influence of Additives of Nanoparticles on Structure Formation of Fine-Grained Hardmetals. *Key Engineering Materials*. 2017, Vol. 743, P. 3–8.

26. Gordeev Yu., Abkaryan A., Binchurov A., Jasinski V., Karpov I., Lepeshev A., Hasanov O., Dvilis E. [Development of effective ways to control the structure and properties of carbide composites modified nanoparticles]. *Journal of Siberian Federal University. Series: Techniques and Technologies.* 2014, Vol. 7, No. 3. P. 270–289.

Библиографические ссылки

1. Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide – A review / Zak Z. Fang [et al.] // Int. Journal of Refractory Metals & Hard Materials. 2009. Vol. 27. Pp. 288–299.
2. Andrievski R. A., Glezer A. M. Strength of nanostructures // Physics-Uspekhi. 2009. Vol. 52, no. 4. P. 315–334.
3. Panov V. S., Zaitsev A. A Trends of development the technology ultrafine and nanosized tungsten carbide WC–Co – A review // Proceedings of the universities. Powder metallurgy and functional coatings. 2014, no. 3. Pp. 38–48.
4. González OliverGonzález Oliver C. J. R., Álvarez E. A., García J. L. Kinetics of densification and grain growth in ultrafine WC-Co composites // Int. Journal of Refractory Metals and Hard Materials. 2016, № 59. P. 121–131.
5. Rempel' A. A., Kurlov A. S., Tsvetkov Yu. V. Tungsten carbide nanopowder for WC–Co hard alloys // Proceedings of the Fourth All-Union Conference on Nanomaterials. M. : IMET RAN, 2011. P. 71.
6. Effects of Cr_3C_2 additions on the densification, grain growth and properties of ultrafine WC–11Co composites by spark plasma sintering / L. Sun [et al.] // Int. J. Refract. Met. Hard. Mater. 2008. Vol. 26. P. 357–361.
7. NbC as grain growth inhibitor and carbide in WC–Co hardmetals / S. G. Huang [et al.] // International Journal of Refractory Metals & Hard Materials. 2008. № 26. P. 389–395.
8. Cholsong P., Ji L., Zhimeng G. Microstructure and properties of ultrafine WC–10Co composites with chemically doped VC // Rare metals. 2011. T. 30, № 2. P. 183–188.
9. Vollath D., Szabo D. V. Coated nanoparticles: A new way to improved nanocomposites // Journal of Nanoparticle Research. 1999, Vol. 1. P. 235–242.
10. Nikolaenko I., Kedin N., Shveikin G. Synthesis of ultrafine powder (W, Ti) C by microwave heating in a stream of argon // International Journal of Materials Research. 2014. Вып. 105, № 12. P. 1232–1235.
11. Essaki K., Rees E. J., Burstein G. T. Synthesis of Nanoparticulate Tungsten Carbide Under Microwave Irradiation // J. Amer. Ceram. Sos. 2010. T. 93, № 3. C. 692–695.
12. High resolution microscopy study in Cr_3C_2-doped WC–Co / T. Yamamoto [et al.] // Journal of Materials Science. 2001. № 36. P. 3885–3890.
13. Powder metallurgy world congress and exhibition / Y. Gordeev [et al.] 1998. Vol. 4. P. 140–146.
14. Gordeev Yu., Abkaryan A., Zeer G. Design and research of cemented carbides and ceramic composites modified by nanoparticles // Advanced Materials. 2012, № 5. P. 76–88.
15. Гордеев Ю. И., Абкарян А. К. Возможности повышения прочности твердосплавных материалов и эксплуатационной стойкости режущего инструмента путем применения термомеханической обработки // Станки и инструмент. 2013. № 3. С. 30–34.
16. Nakamura M., Gurland J. The fracture toughness of WC–Co twoophase alloys: A preliminary model // Metall. Trans. A. 1980. Vol. 11, № 1. Pp. 141–146.
17. Godse R., Gurland J. Applicability of the critical strength criterion to WC–Co // J. Mater. Sci. Eng. A. 1988, Vol. 106. Pp. 331–336.
18. Гордеев Ю. И. [Влияние добавок легирующих керамических наночастиц на структурные параметры и свойства твердых сплавов] / Ю. И. Гордеев [и др.]. Вестник СибГАУ, 2013. Т. 49, № 3. С. 174–181.
19. Конструирование и исследование наноструктурированных твердосплавных композитов с повышенным уровнем прочностных и эксплуатационных характеристик за счет модифицирования наночастицами и термомеханической обработки / Ю. И. Гордеев [и др.] // Вестник СибГАУ. 2014. № 4 (56). С. 209–218.
20. Kurlov A. S. Vacuum sintering of WC–8 wt. % Co hardmetals from WC powders with different dispersity // International Journal of Refractory Metals and Hard Materials. 2011. № 29 (2). Pp. 221–231.
21. Design and Investigation of Hard Metal Composites Modified by Nanoparticles / Y. I. Gordeev [et al.] // Advanced Materials Research. 2014. Vol. 1040. Pp. 13–18.
22. Дворник М. И., Михайленко Е. А. Моделирование процесса распространения трещины в субмикронных и наноструктурных твердых сплавах // Механика композиционных материалов и конструкций. 2014. Т. 20, № 1. С. 3–15.
23. Pattern of the B4C Ceramics Surface Deformation at Local Loading / E. S. Dvilis [et al.] // Advanced Materials Research. 2014. Vol. 872. P. 60–64.
24. Поздняков В. А., Глезер А. М. Структурные механизмы разрушения нанокристаллических материалов // Физика твердого тела. 2005. Т. 47, № 5. С. 793–800.
25. Influence of Additives of Nanoparticles on Structure Formation of Fine-Grained Hardmetals / Y. I. Gordeev [et al.] // *Key Engineering Materials*. 2017. Vol. 743. Pp. 3–8.
26. Гордеев Ю. И. Разработка эффективных путей управления структурой и свойствами твердосплавных композитов, модифицированных наночастицами / Ю. И. Гордеев [и др.] // Журнал Сибирского федерального университета. Сер.: «Техника и технологии». 2014. Т. 7, № 3. С. 270–289.